1989 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

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ON THE SELECTION OF MATERIALS FOR CRYOGENIC SEALS AND THE TESTING OF THEIR PERFORMANCE

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DATE:

August 18, 1989

CONTRACT NUMBER:

University of Central Florida NASA-NGT-60002 Supplement: 2

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by

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ABSTRACT

This report was prepared in support of efforts at the Kennedy Space Center to ensure that accidental leaks of fluids, especially cryogenic fluids, are reduced to a practical minimum. The report begins by addressing three questions: what mission must a cryogenic seal perform; what are the contrasts between desirable and available seal materials; and how realistic must test conditions be? The question of how to quantify the response of a material subject to large strains and which is susceptible to memory effects leads to a discussion of theoretical issues. Accordingly, the report summarizes some ideas from the rational mechanics of materials. The report ends with a list of recommendations and a conclusion.

Key words: Cryogenic seals, constitutive theory, seal assemblies

SUMMARY

A cryogenic seal must control the passage of cryogenic liquids through valves and couplings and must prevent mated parts from damaging each other. In doing so, it must accommodate large changes in absolute temperature. The design of any seal assembly is greatly expedited by the availability of a material that exhibits rubber-like behavior at all operating conditions, is inert to chemical attack, and does not present a fire hazard. No such material is available that meets all of the above requirements in cryogenic applications, so compromises and the diminutions of performance that attend them are difficult to avoid. Various design alternatives, such as fiber reinforced composite seals with a polymer matrix, foam polymers, metal spring-backed seal assemblies, and seals based on the idea of a inner tube filled with helium are discussed.

An example of how the routine installation of a TFE O-ring seal at KSC produced nonlinear strains and memory effects raises the question of how such effects can be quantified. There is a rich literature on the subject and this report includes a synopsis of some of the most important ideas proposed in it.

If the face of a polymer seal is scratched so as to allow a slender channel from the inside to the outside of the pipe it seals, then the rate of flow through that channel is of interest. The mathematical problem of finding the distribution of streamwise velocity across a channel cross section of arbitrary shape is formulated and solutions are presented for cross sections of triangular and semicircular shapes. Formulas for the rate of transport of fluid volume through such channels are then obtained by integration. For the purpose of comparison, these results are set alongside the velocity and flow rate formulas for a pipe of circular cross section.

The recommendations of the study are: (i) that future efforts be directed to the design of seal assemblies rather than the design of solid seals made of virgin plastic; (ii) the development of spring-backed seal assemblies, pneumatic tubes, foams, and fiber reinforced composites should be accelerated; (iii) the statically indeterminate problem associated with stretching of bolts beyond the elastic limit during cooldown of sealed joints should be incorporated into routine practice prior to testing and, if yielding is indicated, steps should be taken (through the installation of spring washers, extra long bolts, spacers, etc.) to eliminate it; (iv) tests should be undertaken to determine whether available foam TFE collapses at the temperature of liquid hydrogen, owing to the liquifaction of gases trapped in its cells; and, (v) some long range testing program (informed by appropriate theory) should be planned and undertaken with the aim of creating an archival literature on seal technology.

The conclusions of the present study are summarized as follows: the mechanical behavior of materials in general and seal materials in particular are captured (if at all) by its constitutive functional; if the material is susceptible

to memory effects and is subject to finite strains (as seal materials are in most designs of seal assemblies), then the constitutive functional can not be represented in terms of a few material constants (such as Young's modulus E, the shear modulus G, the coefficient of thermal expansion α , etc.). Rather, material functions and functionals are involved. Developers of quantitative prediction methods and experimentalists who provide data to support them must face this fact if they are to succeed.

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1. INTRODUCTION

Fuel for the space shuttle main engines is stored in the form of liquid oxygen and liquid hydrogen. These liquids are <code>cryogenic</code>, <code>i.e.</code> at atmospheric pressure, the absolute temperatures at which they boil are small compared to the absolute temperature of the coldest parts of the earth's atmosphere. The act of filling and draining the tanks to contain such liquids necessarily exposes pipes, hoses, valves, <code>etc.</code> through which such liquids are pumped to large changes in absolute temperature. The attendant changes in the geometry of mated parts and the mutual forces between them exacerbate all of the usual problems associated with the control of leaks.

Now the safety of personnel and equipment and the ability of machines to perform their functions can both be compromised by leaks of hydrogen, oxygen, and other fluids routinely pumped through pipes in a launch pad environment. Thus, while leaks of cryogenic materials are hard to avoid in space operations, the level of uncontrolled leaks that one can, in good conscience, tolerate must also be low.

There is little doubt that successful seal technology has been developed and employed in previous space operations undertaken by the United States. There is reason to suppose, however, that much of this technology was developed on an ad-hoc basis and is retained in the minds of experienced personnel, many of whom have left the space program or are planning to do so in the near future. While senior personnel can be encouraged to pass on an much of their best knowledge to junior personnel as they can, and while some of the rest can be developed by the junior personnel, one might hope that at some stage a more abstract, but also more durable, source of knowledge might be created. In this respect, there is a need for an archival literature on seal technology.

In chapter 2, various practical issues on seal technology are raised. Three key questions are posed, i.e. what mission must a cryogenic seal perform; (ii) what are the contrasts between desirable and available seal materials; and, (iii) how realistic must test conditions be if one is to have confidence that a component that performs well in leak tests will perform well in service?

In chapter 3, the discussion turns to theoretical issues. The manner in which a body composed of a given material deforms under load depends upon its history (including its deformation history), the nature of its supports (or, more abstractly, its surroundings) and the intrinsic properties of the material, to name three dependencies. Notwithstanding the availability of standardized tests, the intrinsic properties of a material can seldom, of ever, be measured directly. Normally, they are inferred by substituting measurable parameters (such as the length of a test specimen and its cross sectional area) which are not intrinsic to the material into one or more equations resulting from some theory of material behavior (such as Hooke's law) and solving for certain other parameters (such as Young's modulus) that characterize the material

but may not be directly measurable. Simple theories of material behavior like Hooke's law do not suffice to describe the distortion of a cryogenic seal under typical service conditions. This insufficiency is due to several complications in the nature of that distortion. Thus, however one defines strain, the strains in real seals need not be small. Likewise, however one distinguishes between elastic and inelastic deformations, the deformations in real seals need not be elastic. Among the manifestations of inelastic deformation is the ability of some seal materials to extrude or flow at ambient conditions.

A literature on seal technology will not be archival if it is filled with vague terms. There is, therefore, a need for specific mathematical definitions of deformation history, strain, elastic, solid, fluid, viscoelastic, and other terms relevant to the technology of cryogenic seals. The first main part of chapter three, titled 'Aspects of the rational mechanics of materials', furnishes a primer on terms of this nature as they are used by Walter Noll and Clifford Truesdell in their comprehensive treatise The Nonlinear Field Theories of Mechanics (Reference 1). The second main part of chapter three, titled 'Flow through small holes', is relevant to the prediction of leak rates through a given hole across which a given pressure difference is applied.

Chapters four and five are titled 'Recommendations' and 'Conclusions', respectively. They are summaries in their own right, and so do need further synopsis here.

2. PRACTICAL ISSUES

2.1 GUIDING QUESTIONS

As was stated in the Introduction, this chapter is motivated by three questions, i.e.

- Q1 What mission must a cryogenic seal perform?
- Q2 What are the contrasts betweeen desirable and avialable seal materials?
- Q3 How realistic must test conditions be if one is to have confidence that a component that performs well in leak tests will perform well in service?

Question Q1 is addressed under subheading 2.2 below. Question Q2 is addressed under subheadings 2.3, 2.4, and 2.5, and question Q3 is addressed under subheading 2.6.

2.2 MISSION OF A TYPICAL CRYOGENIC SEAL

A cryogenic seal must control the passage of cryogenic liquids through valves and couplings and must prevent mated parts from damaging each other. It

must, moreover, perform this mission under a variety of constraints. Thus, the changes in the geometry and the mutual contact forces between separate parts of an assembly that attend large changes in absolute temperature must not induce inordinately large stresses within the assembly, nor must they allow gaps to open within it. The hardness of the seal material at cryogenic temperatures must not exceed that of the metal surfaces in touches. Enough toughness of the seal should be retained at cryogenic temperatures so that it does not become inordinately vulnerable to scuffing by adjacent metal parts with small surface defects or to brittle fracture.

2.3 PROPERTIES OF A HYPOTHETICALLY IDEAL SEAL MATERIAL

A seal material is desirable or undesirable accordingly to whether it does or does not expedite the design of valves and couplings. In this sense, the desirablility of a seal material depends upon how many of the following attributes it has:

- A1 It can undergo large-strain deformations elastically over a large temperature range.
- A2 It would be invulnerable to attack by fuels, oxidizers, and other fluids commonly pumped through pipes at KSC.
- A3 It would not exacerbate fire hazards, even when placed in contact with liquid oxygen, nitrogen tetroxide, or other oxidizers.
- A4 It would be soft enough not to scratch adjacent metal parts, but tough enough to resist scratching by them.
- A5 It would be non-porus (i.e. it would not permit seepage of liquid through it).
- A6 It would be inexpensive, easy to form into parts, and commercially available.

2.4 PROPERTIES OF AVAILABLE POLYMER PLASTICS

An extensive collection of physical property data on polymer plastics was compiled in the early 1970's and published as a monograph by the National Bureau of Standards (NBS Monograph 132, Reference 2). According to these data, available polymer plastics may readily be found which possess attributes 2, 3, 5, and 6 above at all temperatures and condition 4 at ambient temperatures.

Most cryogenic seals at KSC are made of Polytetrafluoroethylene (TFE) and its copolymer with Hexafluoropropylene (FEP). According to the authors of Reference 2, FEP has a lower crystalline melting temperature than TFE, which limits the highest service temperatures that parts made from FEP can

stand. On the other hand, fabrication of parts by efficient techniques such as injection molding and extrusion is possible with FEP but not possible with TFE, owing to the lower melting temperature of the former. Fabrication of parts from TFE, by contrast, involves compression of powder. There is little difference between TFE and FEP in other respects, at least as regards the list of attributes cited above. If enough care is taken with respect to design and maintenance, seals made from FEP and TFE may perform satisfactorily under cryogenic conditions. Most of the leaks that do occur appear to be related to the inability of TFE and FEP to meet condition A1 above either at ambient conditions (when it is subject to stress relaxation) or at cryogenic conditions (when it fractures at small to modest strains). Figure 1 represents the temperature dependence of the ductility of three plastics. Here, 'ductility' is defined to be elongational strain at rupture of a test specimen loaded in uniaxial tension. 'Strain' is defined in the one-dimensional engineering sense, i.e. the ratio of the increase in length under load to the unloaded length. Figure 1 shows that at T = 20°K (the normal boiling point of liquid hydrogen) the ductility is less than 0.05. Figure 2 illustrates the results of a uniaxial tensile test of TFE specimens at T = 20°K. three curves show the effects of radiation on the stress-strain diagram. The rightmost curve is the one of greatest interest to this report. It shows that rupture occurs at a tensile strain of 0.032. Regardless of how one classifies the behavior of TFE at this temperature, one can not regard its behavior as rubberlike.

The inability of TFE to spring back to its original shape after a compressive load is removed is illustrated in Figure 3. Each curve corresponds to a particular temperature and includes the stress-strain diagram for loading followed by unloading. The unloading curve does not retrace the loading curve, i.e. compressive loading of TFE exhibits hysteresis. Each time a valve containing a TFE seal is closed or two pipe sections are bolted together with a TFE seal between them, irreversibe work is done in deforming the seal. This circumstance limits the number of times that a valve with a TFE seal may be closed and then reopened without seriously altering the seal geometry. Figure 3 suggests, however, that the hysteresis loop can be reduced to an arbitrarily small size by placing a sufficiently low ceiling on the maximum compresive stress for which the valve seal is rated. Unfortunately, this solves one problem at the cost of creating another. It is a fact of experience that lightly closed valves are more prone to leakage that are tightly closed ones, so there is a conflict between the need to prevent leakage in any one cycle of closing and reopening and the need to extend the useful life of the valve over many such cycles.

The hysteresis effect shown in Figure 3 is one of at least two inelastic effects exhibited by TFE and FEP at ambient conditions that can be gleaned from a perusal of NBS monograph 132. The other effect is stress relaxation. A simple device for testing the stress relaxation of a gasket is illustrated in Figure 4. A metal bolt is presumed to behave according to linear elastic theory and its stress-strain curve is determined experimentally. Once cali-

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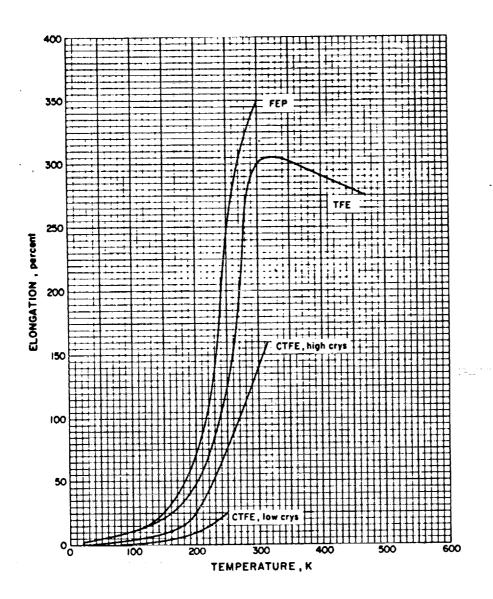


FIGURE 1. Temperature dependence of the ductility of three polymer plastics. Reproduced from Reference 2. Data represent average results from many different investigations.

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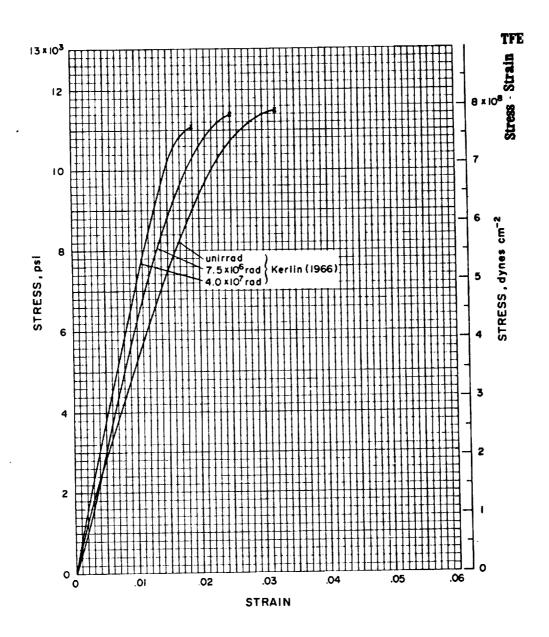


FIGURE 2. Behavior of TFE in a tensile test at 20°K. Data from Kerlin, E.E. and Smith, E.T. 1966 'Measured effects of the various combinations of nuclear radiation, vacuum, and cryotemperatures on engineering materials'. General Dynamics, Ft. Worth MSFC FZK-290. Reproduced from Reference 2.

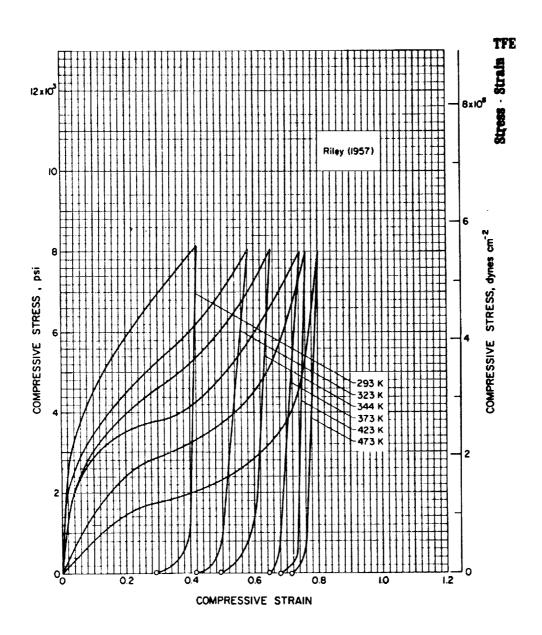


FIGURE 3. Plastic deformation and hysteresis of TFE in compression. Data from Riley, M.W. 1957 'Selection and design of fluorocarbon plastics.' Materials and Methods, Vol. 129. Figure from Reference 2.

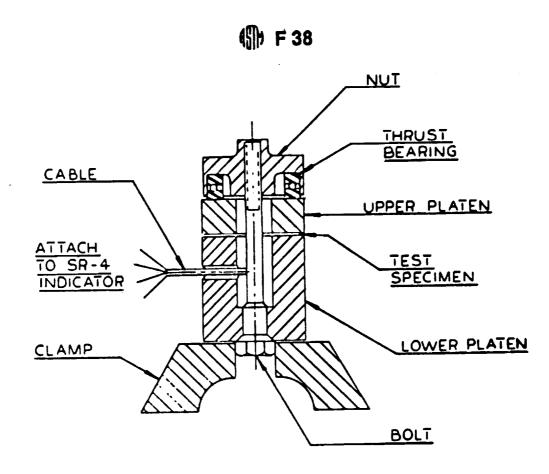


FIGURE 4. Sketch of a Relaxometer, a device for measuring long-term stress relaxation of gaskets. American Society of Testing and Materials, Annual Book of ASTM Standards, 1988.

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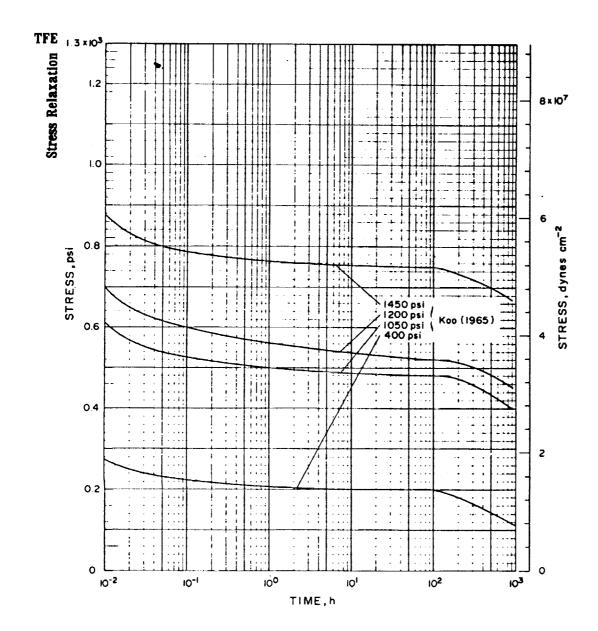


FIGURE 5. Relaxation of compressive stress in a TFE gasket held at constant compressive strain (curve labels indicate *initial* stress). Data from Koo, E.P., Jones, E.D. & O'Toole, J.L. 1965 'Polytetrafluoroethylene as a material for seal applications'. American National Conference on Fluid Power (21st), Illinois Institute of Technology, Chicago. Figure from Reference 2.

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brated, the bolt becomes a gauge for determining the compressive load on the gasket. A gasket may be loaded and the compressive load in it may be recorded at prescribed intervals of time over a period of hours, weeks, or months. Results of some tests of this kind are shown in Figure 5. It is an unfortunate fact that the gasket continues to relax in time after fourty days.

2.5 LIMITATIONS OF UNIFORM MATERIALS AND POSSIBLE ALTERNATIVES

The discussion under subheading 2.4 above indicates that TFE and related polymer plastics are not ideal materials for seal applications. Their most serious limitations, in the context of this report, are (i) hysteresis effects in large-strain compressive loading and unloading at ambient conditions; (ii) long-term stress relaxation at ambient conditions; and (iii) loss of ductility at cryogenic temperatures. The question of whether new compounds can be discovered and developed which exhibit true elastomeric behavior at ambient and cryogenic conditions and which have all of the other attributes listed in subsection 2.3 above can only be addressed by persons having expertise in the field of polymer chemistry, a field outside the present author's competence. There is, however, circumstancial evidence that suggests the degree of difficulty of the problem. Thus, one may argue that the need for a cryogenic elastomer was just as strong in the early days of the space program as it is today. Noting that no such material has appeared in the three decades since the space program began, one might reasonably surmise that the development of a cryogenic elastomer is a difficult task, to be accomplished, if at all, only by talented persons authorized to conduct basic research with few restrictions over a long period of time.

If the prospects of obtaining an ideal cryogenic elastomer are bleak, one is led to ask whether the need for them may be reduced by a design approach which separates functions. Thus, a cryogenic gasket must have variable geometry and must fulfill conditions A2-A6 listed under subheading 2.3 above. Metal springs may be designed to perform elastically over the full temperature range of interest here. Gasket assemblies consisting of thin portions of TFE backed by a metal spring may perform all of the tasks that one would assign to a solid part made from a cryogenic elastomer. Such spring backed gaskets assemblies are, in fact, used in some key couplings in conduits connected to the space shuttle orbiter and their service record (as far as I know) is satisfactory. Spring-backed gasket assemblies are, of course, less simple than gaskets cut out of uniform material and this extra complexity must be viewed as a disadvangage. One may also suppose that the ease with which a spring-backet gasket assembly may be fabricated is a strong function of its size. The smaller is the seal, the greater is the problem of miniaturization.

An alternative approach which fits in with the spring backed concept is one decribed to me by Mr. James Fesmire (DM-MED-4), namely an inflatable seal. The seal resembles an old fashioned inner tube and is filled with a gas like

helium, which does not liquify at the intended service termerature. If the tube membrane is thin enough, then the overall shape of the tube may be altered much more readily than if it were solid (even if it is at cryogenic temperatures). Such ideas should be given serious consideration in the future.

The problem of stress relaxation in polymers may be mitigated, to some degree, through the use of composite materials. Thus, if TFE is reinforced by glass fibers in mat or whisker form, one might expect that slow flow of the polymer would result in slow loading of the glass fibers leading, at length, to a limiting equilibrium state in which the fibers eventually carry all of the load. To illustrate the point, suppose that a pad of fiberglass mat is dipped in oil and then clamped between vise jaws. In equilibrium, the portion of the vise load borne by the oil would be small compared to the part borne by the glass. The nature of this equilibrium might be similar if the matrix surrounding the fibers were TFE instead of oil. Glass reinforced TFE is, in fact, used as seal material at KSC. The present author was furnished with samples of such materals with the trade names Fluorogolde and Fluorogreene. When handled, the most conspicuous feature of these materials is their stiffness. One may surmise that, while mitigating the problem of long-term stress relaxations, these materials exhibit the same problems as uniform polymers with respect to hysteresis in loading and unloading. Indeed, the greater stiffness of these composites may exacerbate the problem of designing joints that retain their tightness to leaks in the presence of large and rapid changes in absolute termperature.

The problems associated with low ductility of TFE at cryogenic temperatures may be mitigated, in part, through the use of foam TFE. The present author was shown samples of a foam TFE material marketed under the trade name GORE-TEX. This material is delivered in tape form with an adhesive backing. It compresses noticably under finger pressure. To be used as a gasket, it must be formed by hand into a ring shape and placed so as to overlap itself. Caps that result at the place of overlap or elsewhere must be wrung out by clamping pressure during installation. Such foam tape exhibits some rebound when subject to compression, but it is by no means elastic. The tightening of joints sealed with such tape results in some extrusion of the material. Of course, such a material would not be suitable as a bearing surface in a valve or other part that is subject to repeated loading and unloading. There is also reason to believe that foam TFE is susceptible to the same phenomenon of long-term stress relaxation as is uniform TFE.

If the gas that fills the microscopic bubbles in foam TFE is one which liquifies at temperatures above that of, say, liquid hydrogen, then exposure of foam TFE to such low temperatures may cause the microscopic bubbles to collapse. If such a collapse did take place on a microscopic scale its effect on a macroscopic scale might be a drastic shrinkage of the seal material. Such an effect would hardly serve the purpose of preventing leaks. One area in which laboratory testing might be especially illuminating is the

response of such foam TFE to immersion in liquid hydrogen. Such tests would, of course, be complicated owing to the difficulty of taking measurements in a liquid hydrogen environment.

The liquifaction at the temperature of liquid hydrogen of the gas used to inflate the bubbles in foam polymers can be avoided by inflating them with gaseous helium. Unfortunately, helium diffuses through TFE quite readily (I am indebted to Mr. Cole Bryan for alerting me to this fact). If, therefore, a foam plastic consisting of microscopic helium balloons were to be formulated, it could not be made of TFE. The problem of finding (or formulating) a material with the requisite impermeability to helium may well be insurmountable, but the possible benefits suggest that the search might be worthwhile.

Seals made of cork are unsuitable for most applications at KSC owing to their vulnerability to chemical attack and to the fire hazard they present (especially in the presence of liquid oxygen). A closed TFE sheath with a cork core may have some features in common with spring-backed gasket assemblies, however, and may even be a realistic option in the case of small seals, in which miniaturization of spring-backed seal assemblies is problematic.

2.6 HOW REALISTIC MUST TEST CONDITIONS BE?

The degree to which one requires that test conditions be realistic depends upon the use one intends to make of data produced by those tests. Thus, if a new valve or coupling is meant to be an exact copy of a proven design, tests should address the question of whether the given test specimen is a faithful replica of its forbears. Checks to determine that the specimen is made of the proper materials and has the correct dimensions and surface smoothness followed by a routine test of leak tightness at ambient conditions may provide adequate confidence that the specimen is in conformity with required specifications. If, alternatively, the test specimen is a prototype of a completely new design, and if the purpose of the test program were to provide assurance that the component will perform well under a variety of critical conditions in service, then a much more exhaustive test program would be called for. The case when a seal assembly is redesigned and retrofitted to existing hardware falls in between these two extremes.

Considering the complicated interactions between changes in geometry and loading that attend large changes in absolute temperature, there is little justification for the hope that simple correlations between leak rates at ambient conditions and leak rates at cryogenic conditions would be reliable except in the most restricted circumstances, i.e. when a separate correlation is developed for each component assembly and history of temperature variations. Thus, cryogenic testing would seem to be an essential part of any component recertification program following any significant change in its design.

Some analytical tools for the prediction of leak rates are desirable, however, even if they are only used in the preparation of test apparatus and instru-

mentation. Some discussion of the problem of predicting the flow of fluid through small holes will be found in subsection 3 of chapter 3 below.

3. THEORETICAL ISSUES

3.1 BACKGROUND

During my first visit to the Propellants and Gases Prototype Laboratory this summer, I was shown the diassembled parts of a twelve-inch aluminum check valve whose purpose was to control the passage of liquid hydrogen. The two major parts of the housing mate along a stepped surface. The exterior corner of one of the steps is bevelled and an O-ring seal is installed in the gap that is formed between the (bevelled) exterior corner and its (unfilleted) interior mate. In a cross sectional view, this gap forms a right triangle. The nominal design at the time it was shown to me specified that the O-ring would be of virgin TFE. Its initial configuration would cause it to fit snugly into the interior corner of its seat. In a meridional plane, its cross section would be rectangular. During installation, then, this rectangular section O-ring is squeezed within an triangular gap.

I was shown a new O-ring and an old one that had been installed, subject to a cryogenic leak test, then removed after disassembly. Some features of the old O-ring were easy to interpret. Thus, the bevelled part of the housing that contains the exterior corner creates a conical surface that flattens one corner of the O-ring. The O-ring takes a permanent set which changes its shape in a meridional cross section in a obvious way. Far less obvious was the permanent set taken by the O-ring with regard to azimuthal expansion. The increase in its overall diameter was at least one half inch. It exhibited a conspicuous slack when placed onto the part of the housing containing the interior corner. Since it fit snugly when new and since installation of the O-ring into the housing did not subject it to any circumferential stretching, a question arises naturally as to what causes this slackening. Mr. Ken Ahmee, who escorted me to the Prototype lab, posed this question to me and I had no ready answer to it.

In studying the literature on the behavior of materials subject to finite strains, however, I did find some references to prior work that touches on similar issues. In 1909, J.H. Poynting (Reference 3) published the results of an experiment on the torsion of a straight wire. According to the equations of linear elasticity, a simple torsional strain of the wire, unaccompanied by any longitudinal compression or tension, should not cause any change in length of the wire. Poynting's results showed that the wire lengthened in response to the twist. He found that the lengthening is proportional to the square of the twist angle, an example of an effect that results from non-linear straining of a material. In later years, Poynting found a way to measure a change in radius of the wire that attends its change in length. He also found that both effects were equally observable and more dramatic when the metal wire was replaced by a rubber rod.

The Poynting effect was independently rediscovered by R.S. Rivlin in 1947 by which time (as pointed out by Clifford Truesdell) Poynting's work was forgotten. The common denominator between the Poynting effect and the slackening of the O-ring described above is a coupling between shear straining in one plane and normal stresses both on the planes that receive the shear stresses and on the plane normal to the plane of the shear.

The number of people who know and care about the Poynting effect, nonlinear strains, normal stresses attendent to them, and the modeling of nonlinear material response in three dimensions with memory has never been large. Those people who have studied such effects have, however, produced a remarkable literature on it. In the hope of identifying those of their insights that are especially relevant to my work this summer, and of laying the foundations for future work, I spent a considerable portion of my time this summer studying that literature. The following section is a synopsis of what I learned.

3.2 ASPECTS OF THE RATIONAL MECHANICS OF MATERIALS

For want of a better term, I will refer to the people whom I described in the last paragraph (namely, those who have relaid the foundations of modern continuum mechanics) as the foundationists. The main structure of their theory is presented in (i) the treatise The Nonlinear Field Theories of Mechanics (Reference 1); (ii) The Foundations of Mechanics and Thermodynamics, Selected Papers by Walter Noll (Reference 4); and (iii) various specialized papers published primarily in The Archive of Rational Mechanics and Analysis. All of the ideas summerized in section 3.2 will be found in the above publications.

3.2.1 BODIES, CONFIGURATIONS, AND MOTIONS. In the formulation of a theory, some ideas must be treated as primative notions, i.e. notions that are not definable in terms of others more primative without engaging in circular reasoning. For present purposes, I will regard terms like time, material point, geometric point, body, mass, and a few others as terms that belong to this class.

Let each material point in a body B be distinguished from each other point in B by a unique material point identifier X. There is often an advantage in replacing this abstract identifier with a definite ordered triple of scalars $\{X_1, X_2, X_3\}$, which may, for example, represent the cartesian position coordinates of the given material point at some reference time. In such a case, the scalars $\{X_1, X_2, X_3\}$ are called the material coordinates of X.

The configuration χ of a body B is a function that maps particle identifiers X to their corresponding geometric positions x, i.e.

$$x = \chi(x)$$
 , $x = \overline{\chi}^{1}(x)$.

The motion of a body B is a one-parameter family χ_t of configurations. The real parameter t here is the time. The above notation is then a shorthand for the more detailed notation

$$x = \chi(x,t) = \chi_t(x) \tag{3.1a}$$

$$x = \bar{\chi}^{1}(x,t) \equiv \bar{\chi}^{1}(x) \qquad (3.1b)$$

3.2.2 STRESS PRINCIPLE AND THE BASIC LAWS. Mechanics is endowed with certain basic laws, four of which may be stated in words as follows:
(i) The mass of a body B is independent of time; (ii) there exists at least one reference frame, an inertial reference frame, relative to which the translational momentum of a body B is constant in time if and only if the resultant force exerted upon it by the surroundings is zero; (iii) the time rate of change of the translational momentum (with respect to an inertial reference frame) of a body B equals the resultant force exerted upon B by its surroundings; and (iv) the time rate of change of the rotational momentum (with respect to an inertial reference frame) of a body B equals the resultant torque exerted upon B by its surroundings. In popular terms, these laws are, respectively, (i) the law of conservation of mass; (ii) Newton's first law; (iii) Newton's second law; and, (iv) the law of moment-of-momentum.

The stress principle of Augustin-Louis Cauchy (1789-1857) asserts (in the paraphrase of Clifford Truesdell, reference 5) that 'upon any smooth orientable surface ∂V , be it an imagined surface in the body or the bounding surface of the body itself, there exists a field of traction vectors $\boldsymbol{t}_{\partial V}$, equi-

pollent to the action of the exterior of ∂V and contiguous to it on that interior to ∂V .' Cauchy's principle, once accepted, permits the resultant force exerted on a body B by its surroundings to be expressed as a sum of two contributions, namely a body force contribution (of which gravitational force is the prime example) and a contribution from contact forces. Let dA represent a differential directed surface area element. Specifically, let |dA| be the geometric area of the surface it represents; let dA be perpendicular to that surface; and let one side of that surface be distinguished by requiring that dA point away from that distinguished side. Let dE be the

differential contact force exerted on dA by its surroundings. Then, in the previous notation,

$$t_{\partial V} = \frac{df_s}{|dA|} .$$

In general $d\mathcal{F}_s$ depends upon both the magnitude and the direction of $d\mathbf{A}$. Let the function T relate $d\mathbf{A}$ to $d\mathbf{f}_s$ at any given \mathbf{x} and t, i.e.

$$d\mathbf{f}_{g} = T(d\mathbf{A}) = T(d\mathbf{A}; \mathbf{x}, t) \qquad (3.2)$$

The laws listed as (ii)-(iv) above may be written, respectively, as follows:

$$\frac{d}{dt}\left(\iiint\limits_{B}\rho\ dV\right)=0\qquad , \tag{3.3}$$

$$\frac{d}{dt}\left(\iiint\limits_{B}\rho \times dV\right) = \iint\limits_{\partial B}T(d\mathbf{A}) + \iiint\limits_{B}\mathbf{b} dV , \qquad (3.4)$$

$$\frac{d}{dt}\left(\iiint\limits_{B} \mathbf{r} \times (\rho \dot{\mathbf{x}}) dV\right) = \iint\limits_{\partial B} \mathbf{r} \times [T(d\mathbf{A})] + \iiint\limits_{B} \mathbf{r} \times \mathbf{b} dV \qquad , \tag{3.5}$$

in which

- (i) ρ , \dot{x} , and \dot{b} are the local instantaneous values of the mass density, material velocity, and body force per unit volume exerted on the material by the surroundings
- (ii) r is the lever arm vector whose head is situated at a material point and whose tail is at the fulcrum relative to which moments are taken.
- (iii) The last of the three equations is restricted to the special case in which all torques exerted on B by the surroundings are moments of forces.

Two operations commute of they can be applied in either order with the same effect. Let $f(\cdot)$ be a function that maps vectors to vectors. Then the action that it exerts on its operand defines an operation. Now $f(\cdot)$ is called a second rank tensor (or tensor, for short) if it commutes with two other operations, namely (i) multiplication by a scalar and (ii) vector addition. Thus, $f(\cdot)$ is a tensor if and only if $f(\alpha x) = \alpha f(x)$ and f(x + y) = f(x) + f(y) for all combinations of vectors x and y and all scalars α . Given

a tensor f, one can define a related tensor from it, denoted f^T and called the transpose of f such that the following identity is satisfied for all combinations of vectors x and y:

$$\mathbf{x} \cdot [f(\mathbf{y})] = [f^{T}(\mathbf{x})] \cdot \mathbf{y} \quad . \tag{3.6}$$

A tensor f is called symmetric if $f^T = f$ and is called skew if $f^T = -f$.

In the 1820's Cauchy proved two fundamental theorems based upon the foregoing concepts which have become pillars of the rational mechanics of materials. They are, first, Cauchy's first stress theorem, which asserts that the function T in (3.2) is a tensor, and Cauchy's second stress theorem, which asserts that T is symmetric. Cauchy's second stress theorem is derived from (3.5) and replaces it in all subsequent analysis.

3.2.3 CONSTITUTIVE EQUATIONS. A dynamical process (according to the definition of the foundationist Walter Noll, cf. reference 6) is a combination $\{T,\chi_t^{}\}$ of a stress tensor T and a motion $\chi_t^{}$ which is compatible with

the basic laws (3.3)-(3.5) (or, more accurately, with the equivalent statements of those laws as differential equations). In the absence of any further assumptions or definitions regarding material behavior, equation (3.4) (or its equivalent statement as a differential equation) could be taken as a formula for computing the body force density $\mathcal D$ for any given combination of present stress $\mathcal T$ and body motion χ_t . Note that the body motion χ_t describes, among other things the full history of the deformation of the body up to the present time. In this (artificial) sense, all combinations $\{\mathcal T,\chi_t\}$ could be regarded as possible dynamic processes. If, however, $\mathcal D$ is imposed, say, by supposing that $\mathcal D$ equals the local gravitational force per unit volume $p\mathcal D$, then there must be other conditions specific to the choice of material of which the body is composed which restrict which combinations of $\{\mathcal T,\chi_t\}$ can be dynamic processes. Such a restriction is called a constitutive equation.

There is a broad class of constitutive equations, each of which serves as a definition of a class of ideal materials, but the class of such constitutive equations is not arbitrary. There are several general principles that all constitutive equations must satisfy to be realistic. Though roots of these general principles may be found in the works of the savants of the previous centuries (like Cauchy), the modern statements of these principles is the work of the foundationists since World War Two (primarily Walter Noll) and it constitutes their primary contribution to our subject. These restrictions on constitutive equations (called axioms) will be presented in section 3.2.5 below after some preliminary remarks are made concerning changes in reference frames.

3.2.4 CHANGES IN REFERENCE FRAME. The representations of objects in mechanics like time, geometric position, direction, etc. are often specific to a choice of reference frame. Thus, if two observers simultaneously record the time at which a given event takes place and if the observers record that time by the unequal numbers t and t*, this inequality need not imply that either observer is wrong in an absolute sense. The two observers may simply be reckoning time relative to different choices of time origin. A similar statement can be made about two different representations, say x and x* that these observers assign to the geometric position of a given point in space. Inequality between x and x* may simply reflect different choices of place origin. Finally, directional notions, such as up, down, left, right, forward, and backward are relative to a particular choice of reference orientation. Thus, if two observers stand beneath a hot air balloon and are asked to describe the direction of its velocity one minute after launch, one (who is facing north) might say that that velocity is 'upward and to the right'; the other (who is facing southward) might describe it as 'upward and to the left'. Both may be correct if due account is taken of the difference between their respective reference orientations.

Fortunately, the list of two origins and one reference orientation upon which representations of mechanical objects may depend is exhaustive. As pointed

out by Truesdell, one may liken a reference frame to a combination of a rigid body and a clock. Reference frames may differ in the manner that a rigid body may be displaced (affecting its place origin and its reference orientation) and its clock may be reset (affecting its time origin), but they may not differ otherwise.

A tensor is called orthogonal (and is normally denoted by the symbol Q) if for all combinations of vectors a and b, the following identity holds:

$$o(\mathbf{a}) \cdot o(\mathbf{b}) = \mathbf{a} \cdot \mathbf{b} \quad . \tag{3.7}$$

One consequence of (3.7) follows from the special case $\mathcal{D} = a$, i.e. $\varrho(a) \cdot \varrho(a) = a \cdot a$. But the dot product of a vector with itself is just the square of its magnitude (distinguished from the original vector by the magnitude marks $| \cdot |$), from which it follows that

$$|\varrho(a)| = |a|$$

for all choices of the vector a whever Q is an orthogonal tensor. In plainer language the vector that serves as input to an orthogonal tensor and the vector that serves as output from it are vectors of the equal magnitude but (possible) different direction.

If, for example, \overrightarrow{XY} represents a vector drawn from a material point X to a material point Y, in a rigid body, then the distance between X and Y must not change as the body is rotated. If x and x denote the representations

xx before and after such a rotation, respectively, then the relation

$$x^* = \varrho(x)$$

implies that $|x^*| = |x|$ (which is consistent with the condition that the body be rigid) but is general in all other respects. In this way, an orthogonal tensor ϱ may represent a rigid rotation.

Truesdell's comparison of a reference frame to the combination of a rigid body and a clock relates to the feature of orthogonal tensors just described. Suppose, for example, that two observers adopt different representations, say $\mathcal E$ and $\mathcal E^*$ of the same force (say the force exerted by an eraser on a desk as it rests under the action of gravity). The representations $\mathcal E$ and $\mathcal E^*$ may differ owing to unequal reference frames adopted by the observers, but the magnitudes $|\mathcal E|$ and $|\mathcal E^*|$ must be equal. Such a relationship is captured by an equation of the form

$$\mathbf{f}^* = \varrho(\mathbf{f}) \quad , \tag{3.8}$$

in which the orthogonal tensor represents the change in the reference orientation between the two frames.

Now the term force is a primative notion in mechanics, i.e. one can not define it in terms of more primative notions without resorting to circular reasoning. Be that as it may, one may list properties always exhibited by

anything one would call a force. Such a property may be called a postulate or axiom. One may note in passing that the foundationists have adopted (3.8) as on of their axioms of forces.

Let x and x^* be two representations of the same geometric point, each referred to a different reference frame. Representations of points, like representations of vectors, may differ under a change of frame owing to a difference between the reference orientations of those two frames. Unlike representations of vectors, however, representations of points may also differ owing to a difference of place origin of those two frames (vectors, remember, are 'free'—they are not specific to the choice of place origin). Following reasoning of this kind, the foundationists argue that the most general transformation between x and x^* under a change of frame may be expressed in the form

$$x^* = c + \varrho(x - q) \quad , \tag{3.9}$$

in which q and c represent the (possibly unequal) place origins in the 'unstarred' and 'starred' frames, respectively. The corresponding general transformation between the representations t and t^* of time in the two frames is

$$t^* = t - a$$
 (3.10)

in which a is a constant.

The laws for transforming representations of velocity and acceleration under a change of frame may be derived by differentiating (3.9) with respect to time, taking due account of the defining features of orthogonal tensors and the possibilities that c, c, and c may themselves be time dependent.

3.2.5 AXIOMS GOVERNING CONSTITUTIVE EQUATIONS. From the foregoing discussion, we may conclude that a change of reference frame $Fr
ightharpoonup Fr^*$ from an unstarred frame Fr to a starred frame Fr^* induces a change in the respective representations of many mechanical objects (e.g. time, force, velocity, etc.). The laws for converting these representations are, however, fixed once ϱ (the change in reference orientation) and the changes in place and time origin are specified.

Enough has now been said to allow us to state three axioms (due to Noll) which must be satisfied by all valid constitutive equations for materials. The first of these is the axiom of determinism:

A1 The (present) stress (at a point) in a body is determined by the history of the motion of the body.

The second is the axiom of local action:

A2 In determining the stress at a given material point x in a body, the motion outside an arbitrarily small neighborhood of that point may be disregarded.

Let $\psi(\varepsilon)$ be any function of time. We introduce the shorthand notation

$$\psi^{(t)}(s) \equiv \psi(t-s)$$
 , $s \ge 0$. (3.11)

Thus, $\psi^{(t)}(s)$ may be called the history up to time t of the function $\psi(t)$ and the parameter s may be regarded as the time lapse. If, as stated in equation (3.1) above, χ_t defines the placement of a body at time t, then we may write its history of placements up to time t as

$$\chi^{(t)}(s,x) = \chi_{t-s}(x)$$
 , (3.12)

in which the function in the right member is the one introduced in (3.1a).

With this notation, the axiom of determinism may be expressed mathematically, i.e. in every kinematically possible process, the stress τ at time t is related to the history of the motion $\chi^{\{t\}}(s,x)$ by an equation of the form

$$T(t) = \int_{s=0}^{\infty} [\chi^{(t)}(s,x)]$$
 (3.13)

The operator \Im is called a constitutive functional. It relates the semi-

infinite family of placements (each of which corresponds to a different value of the time lapse s) to the value of the stress T at time t and does so for every material point X in the body B.

Now the constitutive functional $\overset{\sim}{\Im}$ describes properties intrinsic to the mass s=0

terial of which the body B is composed, and, indeed, all such intrinsic properties are included in it. Thus, for example, any attempt to give a mathematical criterion which distinguishes the fluid from the solid state is ultimately a way of partitioning the various kinds of constitutive functionals that apply to different groups of materials. Similar statements could be made about the difference between elastic and inelastic materials and between materials with memory and materials without it.

Once one accepts that all of the intrinsic features of a material are tied up in its constitutive functional, one is ready to accept the axiom of material objectivity:

A3 If $T \to T^*$ and $\chi^{\{t\}} \to (\chi^{\{t\}})^*$ are the changes in the representations of the present stress and the motion history attendent to a change $F_{T}\to F_{T}^*$ of reference frame, then a constitutive functional \mathfrak{T} that correctly relates variables referred to the unstarred frame must hold equally well (without any change in \mathfrak{T}) when the variables are referred to the starred frame.

Thus, according to this axiom,

$$T = \Re_{s=0}^{\infty} \left(\chi^{(t)}(s,\chi) \right)$$

if and only if

$$T^* = \Re_{s=0}^{\infty} \left([\chi^{(t)}(s,x)]^* \right) . \tag{3.14}$$

In words, axiom A3 states that the material is indifferent to the choice of reference frame a given analysis may make in trying to decribe its properties.

3.2.6 SIMPLE MATERIALS. At this point, the foundationists stop writing equations that hold for all materials and begin to define specific classes of materials. Of these, the first is the <u>simple material</u>. As a prerequisite to its discussion, we must introduce a new concept.

Let κ be function that relates material identifiers x in a body to geometric points, i.e.

$$\mathbf{x} = \kappa(\mathbf{x}) \qquad , \qquad \mathbf{x} = \tilde{\kappa}^{1}(\mathbf{x}) \qquad . \tag{3.15}$$

One may call κ a reference placement of a body. It may happen that a body actually assumes its reference placement at some reference time t_1 , in which case, $\kappa(x) = \chi(x,t_1)$. For the moment, however, we do not introduce this assumption. Now

$$x = \chi(x,t) = \chi[\bar{\kappa}^{2}(x),t] = \chi_{\kappa}(x,t) , \qquad (3.16)$$

in which χ serves much the same purpose as χ , except that now a material point x is identified by its position x in the reference placement κ rather than by the material point identifier x.

Let \mathcal{X}_0 be a fixed point in the domain of χ_{κ} . A motion is called *homogeneous* (relative to the reference placement κ) if there exists a tensor $F_{\kappa}(t)$ [] such

$$\chi_{\kappa}(X,t) = \chi_{\kappa}(X_0,t) + F_{\kappa}(t)[X - X_0]$$
 (3.17)

The above equation is a generalization of the equation of a straight line in the x-y plane, viz. $y(x) = y(x_0) + m(x-x_0)$. The constant m in the straight-line formula corresponds to the tensor F(t)[] (which is a linear operator) in (3.17). In a homogeneous motion (as the foundationists point out) a chain of material points that lie on a straight line when the body is in its reference configuration remain on a straight line in all later configurations.

A material is called simple if the distinction between homogeneous and nonhomogeneous motion does not affect its constitutive equation. Now the operator

F(t)[] in (3.17) is a generalization of the idea of a first derivative. It represents the first derivative of the function that maps $\boldsymbol{\mathcal{X}}$ to $\boldsymbol{\mathcal{X}}$. In different terms, then, the constitutive equation of a simple material involves only the first derivative of the general motion function $\chi_{\boldsymbol{\kappa}}$.

If, in accordance with the rule introduced in (3.12), we denote the history of the gradient $F_{\kappa}(t)[$] up to time t by $F_{\kappa}(t)[$], we have

$$F_{\kappa}^{(t)}(s)[] \equiv F_{\kappa}(t-s)[]$$
 (3.18)

Again, s is the time lapse. The constitutive relation (3.18) then becomes, for a simple material,

$$T(t) = {\overset{\infty}{\otimes}} [F_{\kappa}^{(t)}(s)]$$
 (3.19)

Now simple materials automatically satisfy the principles of determinism and of local action. Further reductions must be undertaken, however, to ensure that (3.19) satisfies the principle of material objectivity.

3.2.7 THE FLUID-SOLID DISTINCTION. The idea of the simple material has led the foundationists to many profound consequences. Limitations of space and scope (as well, of course, as limitations of my own understanding) prevent me from discussing more than two. These are (i) a sharp distunction between the fluid and solid states; and (ii) a framework for the general discussion of stress relaxation and other aspects of fading memory. The distinction between fluid and solid states seems to challenge an intutive notion implicit in the use of the term <code>viscoelasticity</code>, namely that a blurring of the fluid-solid distinction is to be expected when a material exhibits memory. Indeed, the foundationist Walter Noll titled his 1955 thesis 'On the continuity of solid and fluid states.' Three years later, however, he proposed a reorganization of mechanics (reference 6), which includes the fluid-solid distinction just referred to. This later version has permeated all subsequent thinking by the foundationists.

One may call the tensor $F^{(t)}$ defined in (3.17)-(3.19) the deformation history tensor. It is specific to the choice of the reference placement κ [introduced in (3.15)]. There is a chain rule identity that relates the deformation history tensors $F_{\kappa_1}^{(t)}$ and $F_{\kappa_2}^{(t)}$ associated with two different reference reference placements κ_1 and κ_2 , namely

$$F_{\kappa_1}^{(t)} = F_{\kappa_2}^{(t)} P$$
 (3.20)

in which P is a tensor, namely the gradient of the function that maps position in κ_1 to position in κ_2 . To appreciate what P does, one may imagine an ideal experiment for the determination of the constitutive functional in (3.19). Thus, one begins by preparing infinitely many identical test specimens, each of which is a body composed of the material whose behavior is

to be captured by (3.19). Each specimen is subject to a different deformation history which begins with a common reference placement κ_1 . At the end of each history, the stress tensor T of a material point X is found and an ordered pair is formed consisting of the deformation history of that particle and its final stress. The set of all such ordered pairs (which corresponds to the set of all such deformation histories) defined the constitutive

functional @ in (3.19). If the whole sequence of hypothetical experiments s=0

were repeated but with a different choice of initial placement, say κ_2 , then one could not assume, nor could one expect, that the resulting constitutive

functional \mathfrak{G} would be the same as the one that corresponds to the initial s=0

placement κ_1 . There may, however, be special choices of P in (3.20) which represent changes from the reference placement that have no effect whatsoever on the stress. For them and only for them

$$\overset{\infty}{\underset{s=0}{\mathbb{G}}} \left(F_{\kappa_1}^{(t)} \right) = \overset{\infty}{\underset{s=0}{\mathbb{G}}} \left(F_{\kappa_2}^{(t)} \right)$$

or, equivalently,

$$\underset{s=0}{\overset{\infty}{\otimes}} \left(F_{\kappa_2}^{(t)} H_{\kappa_1} \right) = \underset{s=0}{\overset{\infty}{\otimes}} \left(F_{\kappa_2}^{(t)} \right)$$
 (3.21)

[by (3.20)]. A tensor H_{κ_1} that satisfies (3.21) is called a material isomorphism and the set of all such material isomorphisms that begin with the reference placement κ_1 is called the peer group (or isotropy group) belonging to κ_1 . A deformation of material from one reference configuration to another is called unimodular if it does not involve any change in volume. One expects that a change in volume of a body is attended by a change in its internal stresses (especially its internal pressure) regardless of the material of which it is composed. Thus, no peer group contains tensors H_{κ_1} that are not unimodular.

Now the class of unimodular deformations may be divided into two subclasses, namely orthogonal and nonorthogonal. The orthogonal deformations are just those for which H_{κ_1} is an orthogonal tensor [the definition of an orthogonal tensor was given above in the paragraph containing (3.7)]. The orthogonal tensors preserve distances between distinct material points; the nonorthogonal ones do not. Thus, the orthogonal tensors consist of rigid rotations, reflections through a plane, or some combination of the two. The nonorthogonal tensors necessarily involve elongation or contraction of material lines in a body.

If a small sample of solid material is free of residual stresses (however defined), then any effort to subject it to a nonorthogonal unimodular deforma-

tion results in a net alteration of the stresses in it. Note that a material specimen that has residual stresses in it can be subject to a nonorthogonal unimodular deformation that first unloads then reloads the speciman without producing any net alteration of the stress. If, therefore, one is to characterize the solid state by a change in stress that necessarily attends nonorthogonal unimodular deformations, one must include the premise that such deformations begins from a preferred configuration (one that lacks residual stresses).

The foundationists thus propose the following definition of a simple solid:
A simple material is called a simple solid if there exists a reference placement (called an undistorted placement) such that only orthogonal tensors can be members of the peer group associated with that placement.

Fluids, by contrast, have no such preferred configuration. the foundationists definition of a simple fluid amounts to the statement that a simple material is a simple fluid if the peer groups belonging to any two reference placements are the same and are equivalent to the set of all unimodular tensors. Simple fluids may or may not have memory. Indeed, they may have memory of the entire deformation history $F^{(t)}(s)$ that leads to the determination of the present stress. What they forget is the initial configuration κ_1 from which that deformation history $F^{(t)}(s)$, however long, commenced (provided, again, that the deformation history does not change the material volume —fluids do remember overall changes in volume).

3.2.8 FADING MEMORY. The stress tensor at a given material point depends, in general, upon the whole history of deformation of the material in its neighborhood. One may, however, decompose the stress at a point into an equilibrium part and a transient part. As the name suggests, the equilibrium part is the stress that would exist if the material had been in its present configuration forever. This decomposition makes sense only if one has some confidence that the transients die out in time. In somewhat more precise terms, the memory that the material retains of changes of configuration in the near past, as reflected in the present value of the transient part of the stress, is more significant than is the material's memory of changes in the distant past. At the same time, the equilibrium term may reflect changes in configuration that occurred prior to an arbitrarily long time lapse.

The foundationists (cf. reference 1, §§38-41) identify the principle of fading memory with an assumption that the constitutive functional for a simple material is a continuous functional of the deformation history in the neighborhood of the rest history (which corresponds to the history of a body that has been at rest forever).

Now the constitutive functional \mathfrak{G} for a simple material does not operate s=0 on numbers or even on tensors. Rather, it operates upon histories of :

tensors. The mathematical idea of continuity must therefore be expressed in a rather abstract form. Fortunately, such a form is available, although it is technical. Readers interested in the details are referred to reference 1, pp 103-104.

Now continuity of a function imposes a weaker condition upon it than differentiability and differentiability to the order n imposes a weaker condition than differentiability to the order n+1. Thus, the foundationists define a weak principle and a sequence of strong principles of fading memory which impose the conditions of continuity and nth order differentiability, respectively, upon the constitutive functional. If the latter applies, then the constitutive functional may be expanded into a (suitably generalized) Taylor series expansion about the rest history. For a material with fading memory, changes in configuration that occurred in the near past (characterized by a small time lapse s) exert a greater influence upon the transient stress than do changes in configuration in the distant past. This focus on the case of small s leads to a Taylor series expansion of the deformation history $F^{(t)}(s)$ about s = 0. By applying these two Taylor series simultaneously (one of which expands the constitutive functional in a neighborhood of the rest history and the other of which expands the deformation history in the neighborhood of zero time lapse), one obtains a series representation for the transient stress whose terms involve only the present values and the present values of the time derivatives of the deformation history or expressions (such as the rate of strain) derived from it.

The expansion precedure just described is due to Bernard Coleman and Walter Noll (references 7 and 8). Now an expansion is valid in the mathematical sense only if one can estimate the error associated with the approximation that results if the expansion is stopped after n terms. Coleman and Noll keep the same number of terms in the Taylor series for the expansions of the constitutive functional and the deformation history. They show that the error left in stopping the expansion after n terms is proportional to the nth power of α , in which α is a real number in the range $0 \le \alpha \le 1$ and is called the α -retardation of the deformation history. The α -retardation of a given history of deformation $F^{(t)}(s)$ is denoted $F^{(t)}_{\alpha}(s)$ and is defined by

$$F_{\alpha}^{(t)}(s) \equiv F^{(t)}(\alpha t) . \qquad (3.22)$$

If one regards a given deformation history as analogous to a videotape played at a standard speed, then the modified deformation history that results when the given deformation history is played back at a speed slower by a factor α will be analogous to the $\alpha-$ retardation of the given history. The Coleman-Noll expansion represents an approximation within a family of retarded histories. The accuracy of the n-term expansion is greater the more retarded is its history (i.e. the smaller is the α). In the limit of vanishingly small α , the stress reduces to its equibrium value.

A material is elastic if its present stress T is determined by its present deformation $F^{(t)}(0)$ (i.e. the value of $F^{(t)}(s)$ with zero time lapse s). A deformation involves infinitesimal strain if $F^{(t)}(0)$ differs infinitesimally from that of a rigid deformation. Hooke's law of linear elasticity (which, of course forms the starting point of most books on elasticity and most computer programs for stress analysis of three dimensional structures) results from restricting the equations for an elastic material to the case of infinitesimal strains in the Coleman-Noll expansion.

Returning to the case of finite strain, a feature of the Coleman-Noll theory is that the limit $\alpha \! \rightarrow \! 0$ (of infinitely slow deformations) corresponds to the stress distribution of an elastic material. If this elastic material is a fluid, then its stress distribution is that of a frictionless compressible fluid. If one applies the definition of a fluid to the case of slow flow and keeps the the first term in the Coleman-Noll expansion that involves a derivative with respect to the time lapse s of the deformation function $F^{(t)}(s)$ (and ignores the remaining terms, the net contribution from which vanishes with the second power of α), one obtains the constitutive relation for a linearly viscous fluid. This latter approximation is the one upon which the well-known Navier-Stokes equations of fluid mechanics are based (reference 12).

Any constitutive equation for a solid that retains at least one term for the rates [i.e. an s- derivative of $F^{\{t\}}(s)$] is an equation of viscoelasticity. Coleman and Noll use the term finite linear viscoelasticity to describe the special case of the constitutive equation of a simple material that results when the constitutive functional depends linearly upon the deformation history function. In this case, the deformation rates are not necessarily slow. This idealized constitutive equation may be expressed in integral form. Many books on viscoelasticity begin by assuming its validity (or the validity of a one dimensional version of it); see, for example, Viscoelasticity of Polymers by Ferry (reference 9, p 8).

Considering the abstractness of the Coleman-Noll theory, one is hardly surprised that few experimentalists learn enough about it to subject it to a fair test. An experimentalist named H. Markowitz has aquired the necessary knowledge and obtained quality experimental data. His data suggest that the theory of a simple fluid [one which includes all of the dependencies upon history implicit in (3.19) above] is the only theory general enough to permit quantitative agreement with experiments on solutions of polymer plastics in solvents [cf. the monograph Viscometric Flows of Non-Newtonian Fluids by Coleman, Markowitz, and Noll, reference 10, p2]. If a cryogenic seal made of virgin TFE is subject to finite amplitude strains (e.g. extrusion) during installation, one would be optimistic indeed to suppose that the time dependent stresses within it could be described with quantitative accuracy by any theory less general than the Coleman-Noll theory.

Unfortunately, as inclusive as the Coleman-Noll theory is (as of the time reference 1 was written), it is not all-inclusive. In a paper titled 'A New Mathematical Theory of Simple Materials' (reference 11), published in 1972, Noll listed what he called 'at least three severe defects' in his first theory (reference 6, 1958) of simple materials. One defect concerns the dependence of the present stress upon the infinite past (which is not knowable) or upon the recent past (which is not a valid assumption for all materials). A second defect is the failure of the original theory 'to give an adequate conceptual framework for the mathematical description of such phenomena as plasticity, vield, and husteresis.' The third defect concerns Noll's original definition of materials of the rate type (those whose time dependent stresses satisfy a differential equation with respect to time). I have not had the opportunity yet to digest Noll's new theory of simple materials. Suffice it to say, however, that the earlier theory's lack of an adequate conceptual framework for plasticity, yield, and hystereses does not mean these effects are incompatible with it. Rather it means they are not identified explicitly when they occur.

3.3 FLOW THROUGH SMALL HOLES

So far, most of the discussion in this report has been devoted to the mechanics of seal materials. Since a valve or coupling controls the flow of *fluids*, any attempt to predict the rate of transport of fluid volume through a hole resulting from some imperfection or failure of a seal assembly must involve the mechanics of fluids.

An internal document titled 'Metrological Failure Analysis Investigation of the Liquid Hydrogen (LH₂) Leak at Complex 39B' MAB-128-88, dated September 26, 1988 contains photomicrographs of a TFE seal surface after it was removed from an assembly that had leaked. One such photomicrograph is reproduced as figure 6. The largest scratch shown on the figure appears to exhibit a semicircular cross section whose size and shape does not vary appreciably along the midline of the scratch. Such a scratch geometry suggests a fluid dynamics problem. Consider the channel formed between a scratched plastic sealing surface and a flat polished metal plate against which it is pressed. Suppose that this channel extends ultimately from the inside of the pipe to the outside. Let the size and shape of the cross section of the scratch be fixed and let s represent the total arc-length of its midline (defined, for definiteness, as the locus of centroids of the cross sections). Let the scratch be straight or only slightly curved, i.e. the smallest radius of curvature of its midline is large compared to its largest cross sectional diameter D. Let the total pressure drop from the upstream end to the downstream end be a given constant AP. Let the working fluid satisfy the Navier-Stokes equations and have the mass density p and shear viscosity u. The problem,

then, is to find the rate of transport \dot{v} of fluid volume.

The problem of determining the distribution of streamwise velocity across the cross section may be solved mathematically in reasonably simple terms

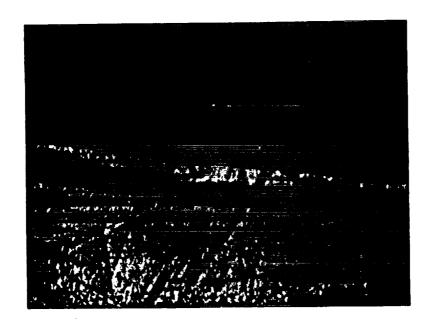




FIGURE 6. Scratches on the surface of a TFE seal (magnification 82X). From 'Metrological Failure Analysis Investigation of the Liquid Hydrogen (LH $_{\rm 2}$) Leak at Complex 39B', NASA/KSC Malfunction Analysis Branch Report MAB-128-88, September 26, 1988, p31.

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if the components of the fluid velocity parallel to the cross sectional planes are uniformly equal to zero and the flow is steady. Under the assumption that all cross sections of the channel are the same, it then follows from the law of conservation of mass (for constant density flow) that the streamwise component u of the fluid velocity for a given point on the cross section is the same for all cross sections.

Let (x,y,z) represent local cartesian coordinates aligned so that the positive x-axis points in the direction of fluid flow. Let (g_{x},g_{y},g_{z}) be the three components of the vector g that represents the local gravitational force per unit mass. Since the scratch can be aligned in any direction, so also can the axes of the coordinates (x,y,z). Since no single coordinate axis in the system (x,y,z) necessarily points 'down', the three components of g relative to it may all be nontrivial. The three components of the velocity vector v relative to these axes are (u,0,0) and v depends only on v and v. The three components of the equations for the rate of change of translational momentum reduce under these assumptions to

$$o = -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial y^2} - \frac{\partial^2 u}{\partial z^2} \right) + \rho g_x$$

$$o = -\frac{\partial p}{\partial y} + \rho g_y$$

$$o = -\frac{\partial p}{\partial z} + \rho g_z$$

Taking p to be a constant and introducing the shorthand

$$p_{ex} = p - \rho(g_x^x + g_y^y + g_z^z) ,$$

the above system becomes

$$0 = -\frac{\partial}{\partial x}(p_{ex}) + \mu \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right)$$

$$0 = -\frac{\partial}{\partial y}(p_{ex})$$

$$0 = -\frac{\partial}{\partial z}(p_{ex})$$

The function p_{ex} (the excess pressure) represents the excess of the actual pressure at a point over what the pressure would be if the fluid were in static equilbrium under its own weight. From the assumption of steadiness and the last two equations, we conclude that p_{ex} depends only on x and

that the first equation reduces to

$$\frac{d}{dx}(p_{ex}) = \mu \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) .$$

For reasons just given, the left member is independent of y, z, and t. Since, however, u is independent of x, the right member has this property. Thus, the common quantity to which both members of the above equation are equal is independent of x, y, z, and t, i.e. it must be a constant K. Thus, we may write

$$\frac{d}{dx}(p_{ex}) = K \tag{3.23}$$

$$\mu \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) = K \tag{3.24}$$

If we assume that no slip occurs between the fluid and the channel wall that enclosed it, we arrive at the boundary condition

to which solutions of the partial differential equation (3.24) are subject.

The best known special case of the problem defined by (3.24) and (3.25) is the case of flow through a smooth-wall circular pipe, first solved by George Gabriel Stokes in 1845 (reference 12). Since the typical cross sectional shape of a scratch is not a circle (at least not a full circle), this well-known solution is useful, at best, only for purposes of comparison with results for more realistic cross sections. As it happens, not much effort is needed to derive the solutions of (3.24) and (3.25) for channels with the cross sectional shape of a semicircle or an equilateral triangle. The mathematical problem defined by (3.24) and (3.25) also arises in the calculation of the distribution of shear stress over the cross section of a prismatic bar subjected to small twist (according to the linear theory of elasticity). The solution for the bar of triangular cross section was found by Adhémar Saint Venant in the last century and is at our disposal for use in the present case.

Consider the triangle shown in figure 7. Let the three sides be numbered 1, 2, and 3 as shown. If O is the centroid of the triangle, then the perpendicular distances from O to sides 1, 2, and 3 are the same. Let this common distance be denoted ℓ . One may also think of ℓ as the radius of the largest circle that can be inscribed in the triangle. Let $m_1, m_2,$ and m_3 be outward unit normal vectors belonging to the three sides as shown. Let m_1 be the position vector of an arbitrary point m_1 in the plane of the triangle relative to its center. Let m_1 be the perpendicular distance from m_2 to side m_3 . Then

$$\ell_n = \ell - y \cdot n_n , \quad n \in \{1,2,3\} . \tag{3.26}$$

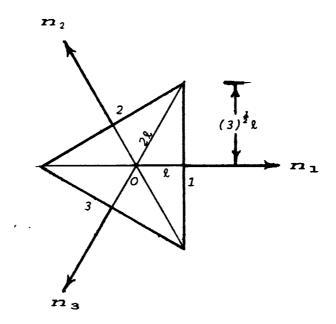


FIGURE 7. Nomenclature for the analysis of the flow through a channel with a triangular cross section.

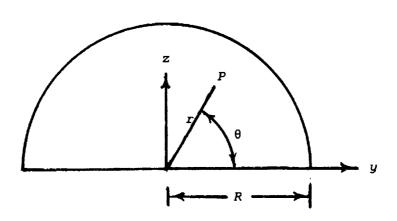


FIGURE 8. Nomenclature for the analysis of the flow through a channel with a semicircular cross section.

Let θ be the angle from m to m reckoned positive counterclockwise. Let $m \equiv |m|$. Then

$$\ell_1 = \ell - r \cos(\theta) \tag{3.27a}$$

$$\ell_2 = \ell - r \cos(\theta + 2\pi/3) \tag{3.27b}$$

$$\ell_3 = \ell - r \cos(\theta - 2\pi/3) \quad . \tag{3.27c}$$

One may relate the polar coordinates (r,θ) to a set of cartesian coordinates (y,z) in the plane of the cross section by the equations

$$y = r \cos(\theta) \qquad , \qquad z = r \sin(\theta) \qquad . \tag{3.28}$$

If P is a point on side n of the triangle, then ℓ_n is zero there. It follows that the product

taken as a general function of position on the cross section, vanishes on all three sides, a condition also satisfied by the function u in (3.24) and (3.25). It is a pleasant surprise to discover that the value of

$$\left(\frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right) (\ell_1 \ell_2 \ell_3)$$

is independent of y and z. It follows that $u \ll \ell_1 \ell_2 \ell_3$ with an appropriate choice of the factor of proportionality, is a solution of the boundary value problem defined by (3.24) and (3.25). The solution, with the factor of proportionality included, may be written in the symmetric looking form

$$u = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) \left(\frac{\ell_1 \ell_2 \ell_3}{\ell_1 + \ell_2 + \ell_3} \right) . \tag{3.29}$$

In terms of polar and cartesian coordinates, the formulas for \boldsymbol{u} take less symmetric looking forms, which, nevertheless, are useful. They are

$$u = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) \left(\frac{\ell^2}{3} - \frac{r^2}{4} - \frac{r^3}{12\ell} \cos(3\theta) \right)$$
 (3.30)

and

$$u = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) \left[\frac{\ell^2}{3} - \frac{(y^2 + z^2)}{4} - \frac{1}{12\ell} (4y^3 - 3(y^2 + z^2)y) \right] \qquad (3.31)$$

Let \dot{v} represent the rate of transport of fluid volume through the channel.

Then \dot{v} equals the integral of u across the cross section. To carry out this integral, the cartesian formula (3.30) for u is most convenient. The result is

$$\dot{v} = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) \ell^4 \frac{9(3)^{\frac{1}{2}}}{20} . \qquad (3.32)$$

The negative signs in (3.29)-(3.31) reflect the fact that $p_{ex}(x)$ decreases in the direction of increasing x, i.e. the fluid flows from higher to lower excess pressure. Thus,

$$\frac{d}{dx}(p_{ex}) < 0 . ag{3.33}$$

It follows that the right members of (3.30) to (3.32) are all positive valued, as, of course, one would expect. In applying the above results, the following facts may be useful:

- (i) The altitude of the triangle equals 32
- (ii) The length of one side of the triangle equals $2(3)^{\frac{1}{2}}$
- (iii) The area of the triangle equals $(3)^{3/2} \ell^{2}$.

The foregoing results apply to laminar flow only. One may define a Reynolds number Re in terms of the fluid velocity u_0 on the centerline and the altitude 3l of the triangle, i.e.

$$Re = \frac{\rho u_0(3l)}{\mu} .$$

The centerline velocity may be evaluated by setting r = 0 in (3.30). The result is

$$u_0 = -\frac{1}{u} \frac{d}{dx} (p_{ex})^{\frac{\ell^2}{3}}$$

Substituting this into our previous formula for the Reynolds number, we have

$$Re = -\frac{\rho \ell^3}{u^2} \frac{d}{dx} (p_{ex})$$
 (3.34)

If Re is of the order of 10^3 or smaller, then one may surmise that the flow is laminar. The flow may be laminar if Re is an order of magnitude higher, but one should not commit onesself to a design decision based upon this assumption without knowledge of other relevant parameters, such as the quality of the inlet conditions, the surface roughness, the presence of acoustical noise and vibration, etc.

Now the channel formed between a polished metal plate and a scratched gasket pressed up against it may or may not have a triangular cross section. Indeed, the photomicrograph of figure 6 suggests that a cross sectional shape having the figure of a semicircle might be more appropriate in that case. The analysis leading up to the problem (3.24), (3.25) may, however, be applied without modification.

Consider the semicircle shown in figure 8. Let (y,z) be cartesian coordinates centered on the midpoint of the straight wall, as shown. Let (x,θ) be the polar coordinates of a point P in the cross section. Let x and y be defined in terms of y and z by

$$y = r \cos(\theta) \qquad z = r \sin(\theta) \qquad (3.35)$$

Let the inside radius of the semicircle be R. If one translates the boundary value problem defined by (3.24) and (3.25) into these coordinates, it requires one to solve the partial differential equation

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 u}{\partial \theta^2} = \frac{1}{\mu}\frac{d}{dx}(p_{ex}) = constant$$
 (3.36)

subject to the boundary conditions

$$(u)_{r=R} = 0$$
 , $(0 \le \theta \le \pi)$ (3.37)

$$(u)_{\theta=0} = (u)_{\theta=\pi} = 0$$
, $(0 \le r \le R)$ (3.38)

One may find a solution of this problem in the form of a Fourier series expansion, i.e.

$$u(r,\theta) = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) R^{2} \left\{ \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)(r/R)^{n} \sin(n\theta)}{(n-2)(n)(n+2)} - \left(\frac{r}{R}\right)^{2} \frac{\sin^{2}(\theta)}{2} \right\} . \quad (3.39)$$

$$(n=odd)$$

The rate of transport \dot{v} of fluid volume corresponding to this u is

$$\dot{v} = \int_{r=0}^{R} \int_{\theta=0}^{\pi} u(r,\theta) r d\theta dr$$

or

$$\dot{V} = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) R^4 \left\{ \left(\frac{8}{\pi} \right) \sum_{n=1}^{\infty} \left(\frac{-1}{(n-2)(n)^2 (n+2)^2} \right) - \frac{\pi}{16} \right\}$$
 (3.40)

There is some arbitrariness in writing the efflux rate formula, particularly in the choice of length parameter. Some standardization can be achieved by expressing squares of the length parameter in terms of the cross sectional area. If one rewrites (3.32) and (3.40) with A as the common symbol to denote the cross sectional area, one obtains

$$\dot{V} = -\frac{1}{\mu} \frac{d}{dx} (p_{ex}) A^2 C_e$$
, (3.41)

in which the coefficient c_e depends upon the cross sectional shape. The following table furnishes the specifics:

Type of cross section	Value of C _e		
	exact	numerical	
triangular semicircular	$(3)^{\frac{1}{2}}/60$ $\sum_{n=1}^{\infty} \frac{-32/\pi^{3}}{(n-2)(n)^{2}(n+2)^{2}} - \frac{1}{4\pi}$ $n = odd$	(2.88675)10 ⁻² (3.01488)10 ⁻²	
circular	<u>1</u> 8π	(3.97887)10 ⁻²	

The efflux coefficient for the circular pipe is included for comparison. If $(p_{ex})_{in}$ and $(p_{ex})_{out}$ denote the inlet and the outlet values, respectively, of p_{ex} , then, under the assumptions implicit in the derivation of the above results, one may take

$$\frac{d}{dx}(p_{ex}) = [(p_{ex})_{out} - (p_{ex})_{in}]/s < 0,$$

in which s is the total arc-length of the channel centerline.

4. RECOMMENDATIONS

I began my work this summer by posing the three questions listed at the start of section 2.1 above, namely (i) what mission must a cryogenic seal perform; (ii) what are the contrasts between desirable and available seal materials; and (iii) how realistic must test conditions be? Later, the scope of my project shifted somewhat. I visited the Propellants and Gases Prototype Laboratory on three occasions, witnessed two cryogenic tests, and (to a modest degree) participated in one of them. After talking with Messers. Fesmire, Popper, and Fox and learning what purposes the tests were meant to serve and what methods were used in them, a fourth question arose, namely (iv) in installing seal assemblies in existing hardware, and, if necessary, redesigning some details, how can one best exploit the advantages and mitigate the disadvantages of available seal materials?

What recommendations I have to make in regard to the first three questions were discussed in section 2.5 above. Thus,

R1 There is much reason to doubt that an ideal elastomeric plastic having the compliance of room temperature rubber and the inertness of TFE

at the temperature of liquid hydrogen can be found or developed. Thus, future efforts should be directed towards the development of seal assemblies rather than solid seal made from virgin plastic.

- R2 In pursuing the implications of R1, the study and evaluation of seal assemblies involving, for example, hollow plastic shells with spring backing, composite seal materials with glass reinforcement, inflatable plastic inner tubes, foam plastic or other alternatives should be accelerated.
- R3 If a bolt joins parts of a coupling made of the same material and if the torque used to tighten the bolt at ambient conditions does not cause it to yield, then the stresses in the bolt may or may not remain below the elastic limit as the assembly is cooled to cryogenic temperatures. Future analyses that precede cryogenic tests (or installation of hardward in service) should address this question. Modification of the installation, e.g. by adding extra long bolts with spring-washers, or spacers, if necessary, should be undertaken to avoid yield of the bolt during cooldown.
- R4 Tests should be undertaken to determine whether the gases that reside within foam TFE (or FEP) do or do not liquify at the temperature of liquid hydrogen and, if so, whether the foam exhibits any tendancy to collapse.
- R5 The tests I witnessed at the Prototype Laboratory emphasized the production of data to support operational decisions. Some future tests should be dedicated to the longer range goal of generating a literature on seal design.

This summer, I was invited to undertake tests of the sort envisaged in R5 above. I refrained from doing so right away, however, owing to the need to study the available literature on the subject, bring the issues into sharper focus, and plan a test program that was cost effective and had a clear sense of direction. Further research proposals by myself or others for support for experiments to be conducted at KSC or my home institution (FIT) may well address R1-R5 in detail.

5. CONCLUSION

Cryogenic and noncryogenic seals at KSC are often subject to finite amplitude strains either in the opening or the closing of valves or the installation of couplings. Polymer seal materials, such as TFE, are subject to various memory effects including hysteresis and stress relaxation. There is no basis for confidence that an analysis of seal mechanics predicated upon the equations of linear elasticity can be quantitative. Only constitutive equations that capture the effects of large strains, three dimensionality, and memory

can succeed in the quantitative analysis of seal mechanics. Functions rather than numbers appear in the quantitative representations of such a constitutive equation. Thus, the attributes of two competing seal materials can not be described with any degree of completeness by a few numbers. To be reliable, future test programs on competing seal materials must face these facts.

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